NATIONAL BUREAU OF STANDARDS REPORT

9390

Progress Report

on

Ionization Constants of Substituted
Benzoic Acids in Ethanol-Water

U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

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By

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The dental research program at the National Bureau of Standards is carried on in cooperation with the Council on Dental Research of the American Dental Association; the National Institute for Dental Research; the Army Dental Corps; the Dental Sciences Division of the School of Aerospace Medicine, USAF; and the Veterans Administration.

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Ionization Constants of Substituted
Benzoic Acids in Ethanol-Water

Abstract

The thermodynamic ionization constants of meta and para
substituted allyl- and propenylbenzoic acids were deter-
mined potentiometrically in aqueous ethanol of varying
ethanol concentration. The pK values increase with in-
creasing ethanol content. The relative acid strength
does not vary with change in solvent concentration ex-
cept for p-propenylbenzoic acid. The $\Delta pK/\Delta\%$ EtOH in-
creases with ethanol content of the medium until a maxi-
mum is reached around 40 wt-% ethanol. A plot of pK +
log $[H_2O]$ versus the reciprocal of the dielectric con-
stant of the solvent gives a nearly linear relationship
to about 44 wt-% ethanol. From pK values found in the
literature a similar linear relationship exists for
other benzoic acids. With the exception of the p-pro-
penylbenzoic acid the σ substituent constants of the
Hammett equation do not change greatly with ethanol
concentration Although σ is solvent dependent for sub-
stituents such as NH_2, OH and NO_2 groups where the elec-
tron distribution is altered because of solvation of the
substituent, for none of these substituents is the depen-
dence of sigma on solvent medium as large as that found
for the p-propenyl group. This behavior may be indica-
tive that the solvation shell surrounding the p-propenyl-
benzoic acid differs from that of the other benzoic acids.

1. Introduction

Previous results [1] have shown that a relationship exists between the
reactivity and the presence of substituent groups in phenols. This rela-
tionship applies to the ionization constants of substituted guaiacols as
well as to the rate of the setting reaction of eugenol and chavibetol with
zinc oxide. One of the objectives of this study was to determine the ioni-
zation constants of meta- and para- allyl- and propenylbenzoic acids. These
constants were determined in aqueous ethanol solutions of varying ethanol
content to study the effect of the composition of the solvent medium on
ionization constants, relative acid strength, solvent-solute interaction,
and the free energy of ionization. Data from this and other investigations
were used to examine the validity of existing relationships between the
dielectric constant of the solvent and ionization constants and to calculate
ion size parameters.

Another aim of this study was to obtain accurate values for the substi-
uent constants of the Hammett equation for allyl and propenyl groups. These
constants may be very valuable in predicting rate or equilibrium parameters
such as chelate stability constants of aromatic compounds containing allyl
or propenyl groups. The results of this and previously published work were
also used to calculate the substituent constants of various functional groups
in aqueous ethanol solutions.

2. Experimental Procedures

2.1 Materials

The benzoic acid and potassium acid phthalate were National Bureau of Standards samples.

The allyl and propenylbenzoic acids were synthesized as previously described [1]. In addition p-propenylbenzoic acid was prepared by isomerization from p-allylbenzoic acid. To 15 ml of a saturated solution of KOH in 90% ethanol, 0.1 g of p-allylbenzoic acid was added in a 50 ml flask. The solution was saturated with argon and refluxed for 48 hours, cooled and neutralized with 1:1 HCl solution. The precipitate was filtered, washed with water, decolorized with activated charcoal, and recrystallized repeatedly from a 30% ethanol-water solution. Yield: 0.04 g (40%) of p-propenylbenzoic acid, MP = 215°C.

2.2 Procedures

The thermodynamic ionization constants at 25.0 ± 0.2°C were determined potentiometrically in an inert atmosphere with a carbonate-free, aqueous ethanol solution of sodium hydroxide in the buffer region where the degree of ionization is between 25% and 75%. Further pH values were obtained in the vicinity of the end point. A Radiometer pH meter with scale expander was used. Before each titration the instrument was standardized with 0.05M potassium acid phthalate (pH = 4.008) and 0.025M $KH_2PO_4 - Na_2HPO_4$ (pH = 6.865).

A 40 ml solution of the acid (2 to 4 x 10^{-3}M) in the respective ethanol-water solution was used in the titrations with the exception of p-propenylbenzoic acid where 100 ml of a nearly saturated solution was employed.

Prior to the titration the solutions were deairated. A slow stream of nitrogen or argon saturated with the solvent used in the titration was passed through the liquid in the reaction vessel for at least 10 minutes. The inert gas was also passed through the solution before each pH reading. All solutions were protected from carbon dioxide contamination by sodium hydroxide-asbestos absorbent. Details of the experimental procedures are given by Brauer, Argentar and Durany [1]. The precise end point was obtained by plotting Δ pH/Δ ml or its reciprocal versus ml of NaOH added and taking as the end point the number of ml of NaOH at which Δ pH/Δ ml is a maximum or Δ ml/Δ pH is a minimum [2]. From the law of mass action and assuming (1) the validity of the Debye-Hückel equation, (2) the activity coefficient of the unchanged, undissociated acid molecule is unity and (3) neglecting the hydroxyl ion concentration the following equation that was employed to calculate pK values can be derived.

$$pK = pH + \log \frac{C_A - ([Na^+] + [H^+])}{[Na^+] + [H^+]} + \frac{A \sqrt{[Na^+] + [H^+]}}{1 + B \sqrt{[Na^+] + [H^+]}} \qquad (1)$$

where $C_A = [HA] + [A^-]$ = total concentration of all acid species [HA] = concentration of the undissociated acid and $[A^-]$ = concentration of anion of the acid. The constants A and B which are dependent on the solvent composition were calculated from the expressions of Bates, Paabo and Robinson [3]: $A = 1.825 \times 10^6 (\epsilon T)^{-3/2}$ and $B = 1.5 (78.3/\epsilon)^{1/2}$ where T = absolute temperature and ϵ = dielectric constant of the solvent which was obtained by interpolation from the values given by Åkerlof [4]. The results were obtained using a Royal Precision computer.

3. Results and Discussion

3.1 Ionization Constants

The thermodynamic pK values of benzoic acid and the substituted benzoic acids in 0 to 64.8 weight percent (0 to 70 volume percent) aqueous ethanol solutions including the number of runs and the standard error of the mean of the pK values are given in Table 1. The standard deviations for pK values obtained during one titration averaged about 0.004 pK units. With increasing ethanol concentration the pK values increase markedly from around 4.2 in water to 6.5 for the 64.8 weight percent ethanol solution. As has been shown by Grunwald [5] $\Delta pK = \log f_{H^+} + \log (f_{A^-}/f_{HA})$ where f_{H^+}, f_{A^-} and f_{HA} are the degenerate activity coefficients of the proton, anion and undissociated acid referred to the infinitely dilute aqueous state. Since ΔpK is a function of both solvent and acid structure and $\log f_{H^+}$ is a function of solvent only, $\log f_{A^-}/f_{HA}$ must at least be a function of acid structure and possibly of solvent.

The activation process for the ionization requires separation of unlike charges and a decrease of the dielectric constant of the medium will decrease ionization because of the greater electrostatic work required in such solvents to form, and separate, two oppositely charged species from a neutral molecule. Furthermore, an increase in ethanol content will change the ion-solvating power of the medium. On increasing the ethanol concentration the nature of the ionization equilibrium is changed, partially because the ethanol-solvated carboxylate differs from the corresponding water-solvated group.

Figure 1 shows the pK values as a function of the ethanol-water composition. For the m- and p-allyl- and m-propenylbenzoic acids the relative acid strength does not vary with solvent concentration and the pK versus ethanol concentration curves have the same general shape. However, p-propenylbenzoic acid is a weaker acid in water than the other benzoic acids, whereas the relative acidity in 64.8% ethanol is considerably higher than that of the other acids investigated. Ion solvating power is the dominant factor in the dissociation of the acids. Increases in the ion solvating power should favor the creation and concentration of charge [6]. Compared to the other benzoic acids investigated, p-propenylbenzoic acid is nearly insoluble in water. Increasing the ethanol concentration increases the solubility very markedly with a resulting increase in relative acid strength. Bonding of ethanol to the π bonds of the p-propenyl group also could enhance the acidic properties. However, if ethanolation occurs the meta propenyl group should exhibit a similar behavior although in this case steric factors may hinder solvation. Evidence that solvation of para substituents may incrase or decrease the acidity of substituted benzoic acids in solvents such as benzene, alcohols, ethylene glycol and dioxane-water have been described by Davis and Hetzer [7].

Kilpatrick [8] has pointed out that estimation of acid strength in mixed solvents such as water and ethanol is difficult since two bases are competing for the proton and two solvated protons may be formed. In addition the solvent dipoles will be oriented differently around the ions and solute molecules. Thus, it is conceivable that a local unmixing of the solvent may occur.

The change in free energy, ΔF, is likely to be a measure of the relative affinity of ion-solvent interaction mainly arising in the primary solvation zone. The ionization constants are directly proportional to the free energy change in the ionization reaction at any given temperature. In Table 2, ΔF, the changes in free energy of ionization for the benzoic acids, calculated from their pK values, are tabulated. The ΔF values increase with increasing ethanol concentration.

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In Table 3 the rate of change of pK with solvent concentration are given. The $\Delta pK/\Delta\%EtOH$ increases with ethanol content of the medium until a maximum is reached around 40 wt-% ethanol. This maximum appears to be in the vicinity of the solvent composition where the nature of the interaction of the binary components of the medium may be altered (so that the benzoate ion becomes more soluble in ethanol than in water) as indicated by the change in the slope of the pK + log [H$_2$O] versus the reciprocal of the dielectric constant (see next paragraph) and where the differential heats of dilution for ethanol reach a minimum [8].

3.2 Ion Size Parameters

The change of free energy, ΔF, on transfer of ions from one solvent medium to another results from a change in the type of solvation shell. The electrostatic part of the free energy change can be estimated by the Born equation [10], if the ions are treated as spheres of finite radius r immersed in a continuum of uniform dielectric constant ϵ. Plots of pK versus the reciprocal of the dielectric constant are not linear since the Born equation does not take into account the specific interaction between ions and the solvent which must contribute significantly to the nonelectrostatic part of the free energy change. Yasuda showed that linearity of the pK versus $1/\epsilon$ plot is improved for partially aqueous solvents by the addition of a water concentration term to account for the variation of the amount of water in the mixed solvent [11]. With the exception of media containing high concentrations of organic solvents the acids investigated had almost the same dissociation constants in various mixed solvents with the same dielectric constant.

Shedlovsky [12] assumes that in mixed solvents such as ethanol-water, on dissolving a weak organic acid the following reactions take place:

$$HA + H_2O \xrightleftharpoons{K_1} HA \cdot H_2O \xrightleftharpoons{K_2} H_3O^+ \cdot A^- \xrightleftharpoons{K_3} H_3O^+ + A^- \tag{2}$$

$$HA + ROH \xrightleftharpoons{K_4} HA \cdot ROH \xrightleftharpoons{K_5} ROH_2^+ \cdot A^- \xrightleftharpoons{K_6} ROH_2^+ + A^- \tag{3}$$
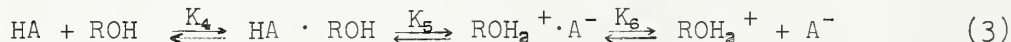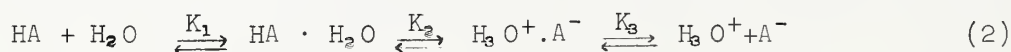
where K_1 to K_6 are the corresponding mass action constants. The overall constants for each solvent are K_H and K_R where

$$K_1 \; K_2 \; K_3 \; = \frac{[H_3O^+] \; [A^-] \; f^2}{[HA] \; [H_2O]} \; = K_H \tag{4}$$

$$K_4 \; K_5 \; K_6 \; = \frac{[ROH_2^+] \; [A^-] \; f^2}{[HA] \; [ROH]} = K_R \tag{5}$$

Assuming that the concentrations of all the electrically neutral species can be taken as their activities and that the last step in the ionic dissociation is controlled by simple coulombic forces, then

$$K_H = B_H \; e^{-b} \tag{6}$$

$$K_R = B_R \; e^{-b} \tag{7}$$

where B_H and B_R are empirical constants; $b = e^2/\epsilon kTa$ in which e is the electronic charge, k is the Boltzman constant, T is the temperature in degree K. The parameter, a, may be interpreted as the distance between the centers of charge in the ion-pairs when the ions are in contact. It can be shown that if

$$B_H \gg B_R, \; pK + \log [H_2O] + \log B_H = \frac{1}{2.303} \; \frac{e^2}{k \; T \; a} \; (\frac{1}{\epsilon}) \tag{8}$$

thus a plot of pK + log [H$_2$O] against $1/\epsilon$ should be linear (at least in the

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water rich region of solvent composition) and the ion size parameter, a, can be obtained from the slope. For acetic acid in water-ethanol, the linear relationship applies up to nearly 50 weight percent (28 mole%) ethanol [12].

On plotting pK + log [H_2O] versus $1/\epsilon$ for the benzoic acids investigated, a nearly linear relationship was obtained from 0 to 44 weight percent ethanol. The values of a and -log B_H (the intercept on the ordinate when $1/\epsilon$ = 0) and their estimated standard deviations were obtained by the method of least squares and are given in Table 4. The ion size parameter and the -log B_H values for the benzoic acids are the same within experimental error with the exception of p-propenylbenzoic acid. Unexpectedly, the ion size parameter for acetic acid is 2.56 Å [12] which is considerably larger than the values obtained for benzoic acid in this study. It is conceivable that the larger ratio of charge to mass of the acetate ion compared to the benzoate ion may lead to an increase in hydration.

To check further the validity of the pK + log [H_2O] versus $1/\epsilon$ relationship, literature values of the ionization constant of benzoic acid in ethanol-water were collected and plotted in Figure 2. The values of Bright and Briscoe [13] were corrected by equation 1 where pH was taken as the observed pH and the second term was omitted since it was found to be negligible. The value of [Na^+] was 0.01 mol/l and the [H^+] terms were neglected. The volume percent ethanol was converted to weight percent for the pK values of Bright and Briscoe [13] and Tabagua [14]. The values of Grunwald and Berkowitz as given in reference 5 were also plotted in Figure 2. The earlier values given in the literature [15, 16] were not used since it was either impossible to calculate the exact weight percentage of ethanol or not enough data were available to calculate the thermodynamic ionization constants. Up to 45 weight percent ethanol, the thermodynamic pK values are in good agreement despite the fact that in Grunwald's and our work, glass electrodes were used whereas Tabagua, and Bright and Briscoe employed hydrogen-AgCl and hydrogen-calomel electrodes respectively. At concentrations exceeding 80 wt-% alcohol the differences in the pK values are considerable. A possible cause for this discrepancy is that the glass electrode may not always measure hydrogen ion activity accurately at high ethanol concentrations. The nearly linear relationship of pK + log [H_2O] versus $1/\epsilon$ up to 45 wt-% ethanol is clearly seen from Figure 2. A similar relationship exists for anisic acid (p-methoxybenzoic acid) (also plotted in Fig. 2) the pK of which was accurately determined by Sager and Bower [17] and for the eight substituted benzoic acids studied by Bright and Briscoe [13]. The approximately linear relationship up to around 45 wt-% is not unexpected since the molar concentration of water in this region is always much larger than that of ethanol. In view of the larger dipole moment of water compared to ethanol, preferential hydration of the substituted benzoate ions should occur and, therefore, their effective diameter should be practically constant over a considerable concentration range. On increasing the ethanol concentration, substitution of water by ethanol, in the solvent cloud surrounding the substituted benzoate ion takes place. It would be interesting to determine if a transition from the hydrated ion to an ethanol solvated complex takes place around 45 wt-% ethanol.

3.3 Hammett Sigma Constants

Among the linear free energy relationships the equation first proposed by Hammett has been very successful for correlating rate and equilibrium constants. This equation describes the effect of a meta or para substituent on the rate or equilibrium constant of an aromatic side chain reaction provided that the resonance interaction between the substituent and the reaction center is either small or proportional to the polar effects.

For acid dissociation equilibria, the Hammett equation may be written:

$$pK_0 - pK = \sigma\rho \qquad\qquad (9)$$

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where pK_0 and pK are the negative logarithms of the ionization constants for the corresponding unsubstituted compound and the meta or para substituted benzene derivative respectively, σ is a substituent constant which is a measure of the ability of the substituent to donate or withdraw electrons and ρ is the solvent-dependent reaction constant characteristic of the side reaction under consideration. The reaction constant ρ has been defined as unity for the acid dissociation equilibrium of benzoic acid in water at 25°C so that σ can be defined as the difference between the logarithm of the ionization constant in water of the substituted benzoic acid and benzoic acid itself.

Only limited data are available on the change of sigma or rho with solvent. For ethanol-water systems Grunwald and Berkowitz [5] showed that

$$\rho = \rho^W + \beta Y_- \tag{10}$$

where ρ^W is the reaction constant which by definition is 1.000 for benzoic acids and its derivatives in water, Y_- is a solvent dependent activity function and the parameter $\beta = 0.628$. By interpolation of the data given in reference 5 values at the respective weight concentrations of ethanol were found and the corresponding ρ values were calculated. These rho values are in reasonably good agreement with other values given in the literature for the ethanol concentrations investigated [18-20].

It is interesting to note that up to 45% ethanol content the product of ρ and ϵ is constant within ± 2.3%. According to Bowden [21]

$$\rho = (A + B/\epsilon)/RT \tag{11}$$

where the constants A and B respectively describe the susceptibility of the reaction to polar effects independent of and dependent on the medium. If A is negligible compared to B/ϵ then ρ is inversely proportional to ϵ. In the 0-45 wt-% ethanol range where the reaction constant varies inversely with the dielectric constant of the medium any effect caused by preferential solvation of the anion or the undissociated acid by the two solvents appears to be negligible.

Using the calculated ρ values, the sigma values of the Hammett equation were obtained and are tabulated in Table 5 and plotted in Figure 3. With the exception of the p-propenylbenzoic acid the σ values do not change greatly with change in ethanol concentration. The σ values for the p-propenyl group are strongly solvent dependent (-0.27 in water and 0.27 in 64.8 wt-% ethanol) and may go through a minimum in the neighborhood of 12 wt-% ethanol. It is likely that the solvation shell surrounding the p-propenylbenzoic acid differs from that of the other benzoic acids. To check further the effect of solvent composition on σ the corrected pK values of Bright and Briscoe [13] and rho constants obtained by the equation given by Grunwald and Berkowitz [5] were used to calculate σ for ten substituents. These data including the estimated standard deviation of the sigma values for all ethanol concentrations are given in Table 6. The substituent constant is markedly dependent on solvent for the NH_2, OH and NO_2 group only, where the electron distribution is altered because of solvation of the substituent. However, for none of these substituents is the dependence of sigma on solvent medium as large as that found for the p-propenyl group in this study. This behavior may be indicative that the solvation shell surrounding the p-propenylbenzoic acid differs from that of the other benzoic acids.

The ionization constants for benzoic acids are recommended for calculating primary Hammett substituent constants [9]. This is especially true for the p-propenyl group since p-propenylphenol is not very stable in basic media. A comparison of the secondary sigma constants determined previously from the pK values in water of guaiacol and substituted guaiacols [5], and the primary constants obtained from the respective benzoic acids are given in Table 7. These values for the allyl groups agree within ± 0.02. For the

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m-propenyl group the sigma constant decreases by 0.08 when benzoic acids are used instead of guaiacols. The greatest change in sigma occurs for the p-propenyl group (sigma values are 0.05 and -0.28) as calculated from the pK's of guaiacols and benzoic acids, respectively . In p-propenylguaiacols the propenyl group is in direct conjugation with the acidic OH whereas in the corresponding benzoic acid any resonance effect of the propenyl group is transmitted to the para carbon atom of the ring and then transmitted to the acidic -OH group by induction.

4. Summary

The thermodynamic pK values of allyl- and propenylbenzoic acids in aqueous ethanol increase with increasing ethanol content. The pK values are dependent on the dielectric constant of the medium. For mixed solvents up to 44% water an approximately linear relationship between pK + log [H_2O] and dielectric constant exists. The Hammett sigma substituent constants for the m- and p-allyl and m-propenyl groups do not vary greatly with composition of the solvent. For the p-propenyl group the sigma constant is greatly affected by the medium; this solvent dependence is larger than that for other groups.

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Table 1

pK Values of Substituted Benzoic Acids
in Aqueous Ethanol Solution

Temperature = 25.0 ± 0.2°C

| Substituent | Weight Percent Ethanol in Solution | | | | | | | | | | | | | | |
| | 0.0 | | | 12.2 | | | 25.2 | | | 44.1 | | | 64.8 | | |
	n	pK	$S/\sqrt{n}$[a]	n	pK	$S/\sqrt{n}$[a]	n	pK	$S/\sqrt{n}$[a]	n	pK	$S/\sqrt{n}$[a]	n	pK	$S/\sqrt{n}$[a]
Hydrogen	17	4.210	.002	14	4.444	.002	16	4.918	.003	8	5.692	.004	9	6.439	.005
m-Allyl	9	4.266	.004	8	4.514	.007	4	5.035	.010	5	5.808	.003	4	6.532	.009
p-Allyl	9	4.326	.004	8	4.563	.003	5	5.061	.007	3	5.811	.003	3	6.537	.013
m-Propenyl	5	4.248	.006	7	4.485	.007	4	4.972	.001	7	5.763	.008	2	6.478	.008
p-Propenyl	4	4.487	.003	3	4.785	.039	4	5.154	.016	2	5.842	.003	2	6.011	.008

[a] Standard error of the mean = $\dfrac{S}{\sqrt{n}}$

$$S = \sqrt{\frac{\Sigma_i (X_i - \overline{X})^2}{n-1}}$$

n = number of runs

Table 2

ΔF Values for the Dissociation of Substituted
Benzoic Acids in Aqueous Ethanol Solutions
Temperature: 25.0 ± 0.2°C

Wt.% Ethanol	ΔF in cal/mole Substituent				
	H	m-allyl	p-allyl	m-propenyl	p-propenyl
0	5744	5821	5902	5796	6122
12.2	6063	6159	6226	6119	6529
25.2	6710	6870	6905	6784	7032
44.1	7766	7924	7929	7863	7971
64.8	8785	8912	8919	8839	8201

Table 3

Change of pK Values of Substituted
Benzoic Acids with Solvent

$(\Delta pK)_{EtOH}/\Delta\%EtOH$

Substituent	0-12.2%	12.2-25.2	25.2-44.1	44.1-64.8
Hydrogen	1.92×10^{-2}	3.65×10^{-2}	4.10×10^{-2}	3.61×10^{-2}
m-Allyl	2.03×10^{-2}	4.01×10^{-2}	4.09×10^{-2}	3.50×10^{-2}
p-Allyl	1.94×10^{-2}	3.83×10^{-2}	3.97×10^{-2}	3.57×10^{-2}
m-Propenyl	1.94×10^{-2}	3.75×10^{-2}	4.19×10^{-2}	3.45×10^{-2}
p-Propenyl	2.43×10^{-2}	2.84×10^{-2}	3.64×10^{-2}	0.82×10^{-2}

Table 4

Ion Size Parameters and Values of $-\text{Log } B_H$
for Benzoic Acids

Substituent	Ion Size Parameter	$-\text{Log } B_H$
	Å	
Hydrogen	1.25 0.10[a]	3.46 0.17[a]
m-Allyl	1.19 0.07	3.40 0.18
p-Allyl	1.25 0.07	3.57 0.17
m-Propenyl	1.22 0.06	3.43 0.15
p-Propenyl	1.44 0.10	4.10 0.18

[a] Estimated standard deviation

Table 5

Hammett Sigma Constants

Ethanol Concentration	ρ[a]	m-Allyl		p-Allyl		m-Propenyl		p-Propenyl	
Wt %									
0	1.000	-.056	.004[b]	-.116	.004[b]	-.038	.006[b]	-.277	.023[b]
12.2	1.128	-.062	.006	-.105	.003	-.036	.006	-.302	.035
25.2	1.266	-.092	.008	-.113	.006	-.043	.002	-.187	.013
44.1	1.465	-.079	.003	-.081	.003	-.048	.006	-.102	.003
64.8	1.578	-.059	.007	-.062	.009	-.025	.006	+.271	.006

[a] Calculated from ρ = 1.000 + 0.628 Y_-, where Y_-, which is a characteristic parameter of carboxylate-carboxylic acid equilibria, was obtained by interpolation of the values given by Grunwald and Berkowitz [5].

[b] Standard deviation = $\sqrt{\dfrac{S^2_{pK_H} + S^2_{pK_S}}{\rho}}$

where S_{pK_H} is the standard error of the mean for benzoic acid and S_{pK_S} is the corresponding value for the substituted benzoic acid.

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Table 6

Sigma Constants for Various Substituents[a]

Sigma Constants

Wt % ETOH	ρ	m-CH₃	p-CH₃	m-NH₂	pNH₂	m-OH	p-OH	m-Cl	p-Cl	m-NO₂**	p-NO₂**
0	1.00	-0.07	-0.19	-0.61	-0.74	0.14	-0.32	0.37	0.14	0.72	0.78
16.5	1.17	-0.12	-0.31	-0.42	-0.64	-0.05	-0.42	-	-	-	-
34.4	1.36	-0.04	-0.11	-0.13	-0.55	0.05	-0.30	0.38	-	1.13	1.04
44.1	1.46	-0.05	-0.11	-0.13	-0.54	0.02	-0.29	0.36	0.30	0.77	0.88
64.8	1.58	-0.10	-0.08	-0.18	-0.60	-0.08	-0.35	0.33	0.27	0.75	0.85
75.9	1.60	-0.09	-0.08	-	-0.62	-0.08	-0.39	0.34	0.30	0.71	0.81
87.7	1.61	-0.14	-0.11	-	-0.66	-0.12	-0.47	0.33	0.26	0.67	0.77
93.7	1.62	-	-	-	-	-	-	-	-	0.82	0.90
100*	1.63	-0.14	-0.14	-	-0.66	-0.13	-0.48	0.34	0.28	0.86	0.96
Average		-0.09	-0.14	-0.29	-0.63	-0.03	-0.38	0.35	0.26	0.80	0.87
Estimated standard deviation		0.04	0.08	0.21	0.06	0.09	0.07	0.02	0.06	0.15	0.09

* From extrapolated pK values.

** Uncorrected pK values using quinhydrone electrode for benzoic acid and substituted benzoic acids.

[a] Calculated from Bright and Briscoe [13].

Table 7

Sigma Values of Allyl and Propenyl Groups

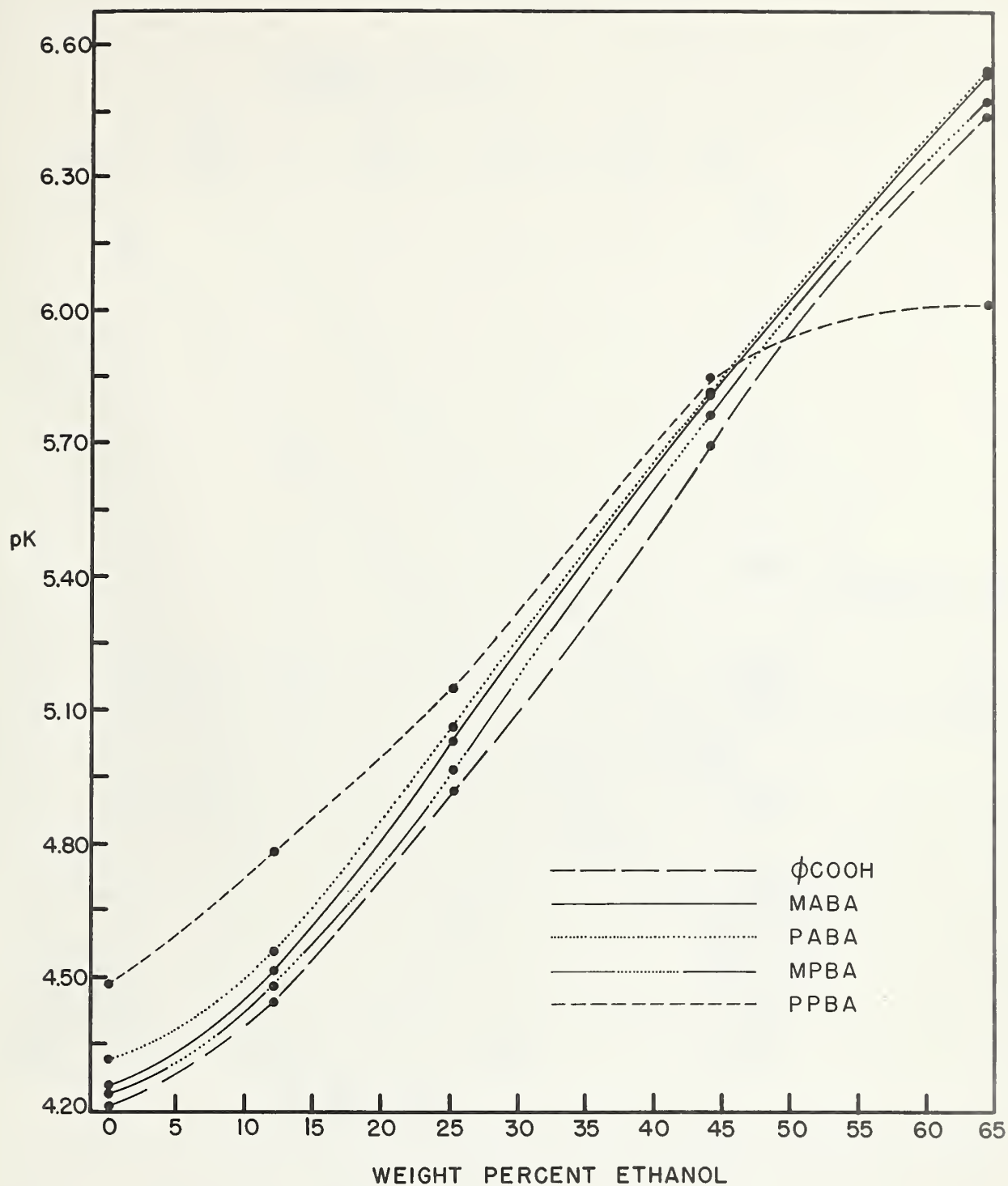| Substiuent	Sigma	
	Primary[a]	Secondary[b]
m-Allyl	-0.056	-0.02
p-Allyl	-0.116	-0.10
m-Propenyl	-0.038	+0.04
p-Propenyl	-0.277	+0.05

[a] From benzoic acids

[b] From guaiacols

Figure 1. Change of ionization constants of benzoic acid
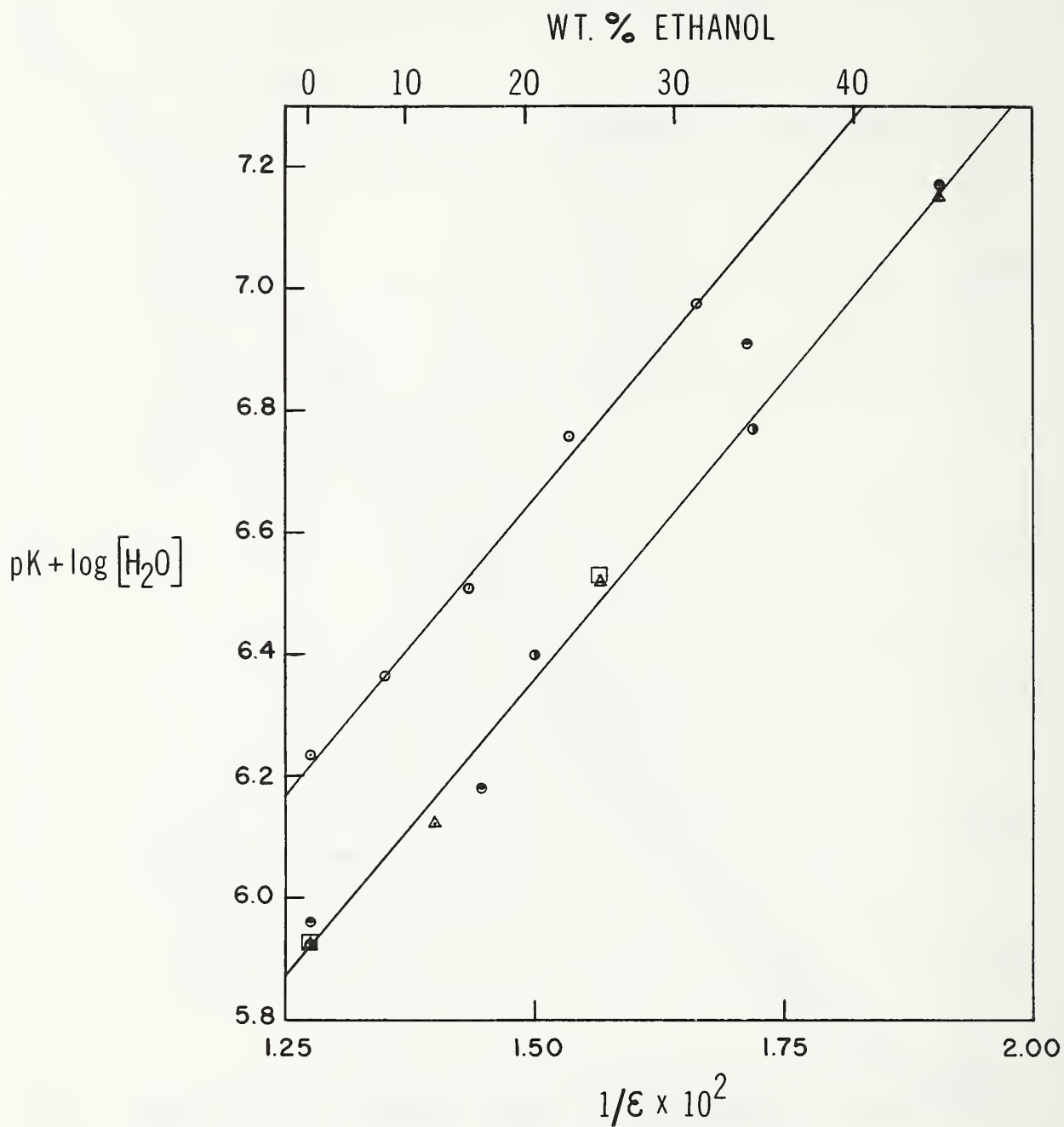with change in ethanol content of the solvent.

Figure 2. Plot log pK + log [H₂O] versus 1/ε. Benzoic acid: △ this study, ◑ Grunwald and Berkowitz [5], ◕ Bright and Briscoe [13], ▢ Tabagua [14]. Anisic acid: ⊙ Davis and Hetzer [9].
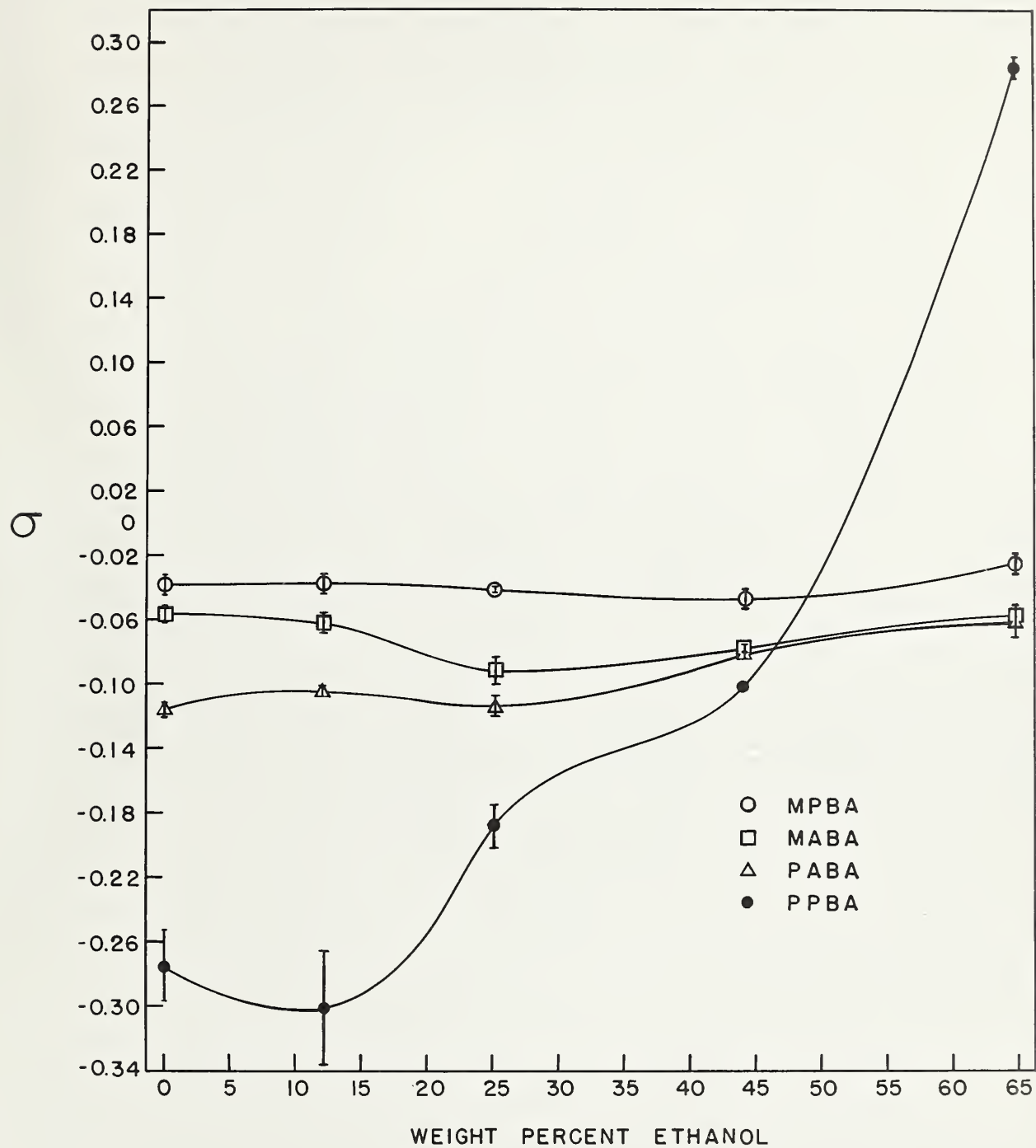
Figure 3. Change of sigma substituent constant with ethanol concentration.